Letters to the Editor

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Modulation effects in NMR.

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While observing NMR absorption lines, it is the usual practice to modulate the absorption line with a sine wave of suitable amplitude and the resulting AC signal whose amplitude is proportional to the first derivative of the line shape function $g(h)$ is recorded where h is the value of the magnetic field from the resonance value. The purpose of this note is to show the effect of different types of modulation on the strength of the signal that is recorded.

Let the modulation employed be $f(t)$ ... (1)

The out-put is proportional to $g'(h)[h+f(t)]$ ... (2)

where $g'(h)$ is the first derivative of $g(h)$ and $h = H-H_0$

Let $g(h) = ph$ ... (3)

where p is a constant (*i e*, we assume that the portion of the line traversed by the modulation is linear).

If we use a phase sensitive detector, the out-put v of the PSD is proportional to the coefficient of sin ωt in (2).

Let us asume that $f(t)$ the modulation used has a periodicity ω. Then,

$$f(t) = a_0+a_1 \sin \omega t+a_2 \sin 2\omega t+a_3 \sin 3\omega t+a_4 \sin 4\omega t+a_5 \sin 5\omega t \quad \ldots (4)$$

Expressing sin $2\omega t$, sin $3\omega t$ etc in terms of sin ωt, we get

$$f(t) = a_0+\sin \omega t[(a_1+3a_3)+\cos \omega t(2a_2+4a_4)-4a_3 \sin^2 \omega t+5a_5\cos^2\omega t- 8a_4 \cos \omega t \sin^2 \omega t-8a_5 \sin^2 \omega t \cos^2\omega t-7a_5 \sin^2 \omega t+8a_5 \sin^4 \omega t$$

Replacing terms within brackets by their averages, we find,

$$v = k(a_1+a_3+a_5) \quad \ldots (5)$$

where k is a constant.

Special cases: If we use a full square-wave modulation of frequency ω and amplitude h_m we can write,

$$f(t) = \frac{4h_m}{\pi} [\sin \omega t+1/3 \sin 3\omega t+1/5 \sin 5\omega t+\ldots$$

$$\therefore \quad v = \frac{322}{165} (kh_m).$$

In a similar way we can show that, v is $= kh_m$ for sinusoidal modulation, $\frac{161}{165}(kh_m)$ for half square-wave modulation and $\frac{80.5}{165}(kh_m)$ for saw-tooth type of modulation. Thus we find that we get the strongest signal if we use a full square-wave modulation.

It is enough to consider the first four or five terms in (4) because the different types of modulation that we are thinking of happen to be represented by fairly fast converging Fourier series. But care must be taken to see, while employing square-wave modulation, that ω is small so that 5ω is not large enough to affect the steady state assumptions made in the theory.

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Vibrational spectra of o- and m-methylstyrenes

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Styrene is one of the important organic compounds which has attracted the attention of a large number of workers The infrared, Raman and electronic spectra of styrene have been studied thoroughly by Stair & Colbelt (1935), Williams (1936) and Pitzer *et al* (1946). The infrared absorption spectra of its halogenated derivatives and electronic absorption spectra of the three isomeric methylstyrenes have been studied by Ansari (1968). But in the case of its methyl substituent, no work on infrared and Raman spectra has been reported so far. The present note deals with the infrared spectra of *o*- and *m*-methylstyrenes.

The compounds of L.R. grade quality were supplied by Koch-Light Laboratories, U.K. The infrared traces of the compounds were recorded in the liquid phase on a 13U Perkin Elmer double beam infrared spectrophotometer equipped with NaCl prism using a cell of thickness 0.05 mm.

Both the molecules belong to the C_s symmetry with the molecular plane as the only symmetry element when we assume the vinyl and methyl groups behaving as a single atom. The 51 normal modes of vibrations are divided as 35 a' (planar) and 16a'' (non-planar). All the vibrations are allowed in infrared and Raman spectra.